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Runoff sources and land cover change in the Amazon: an end-member mixing analysis from small watersheds

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Abstract The flowpaths by which water moves from watersheds to streams has important consequences for the runoff dynamics and biogeochemistry of surface waters in the Amazon Basin. The clearing of Amazon forest to cattle pasture has the potential to change runoff sources to streams by shifting runoff to more surficial flow pathways. We applied end-member mixing analysis (EMMA) to 10 small watersheds throughout the Amazon in which solute composition of streamwater and groundwater, overland flow, soil solution, throughfall and rainwater were measured, largely as part of the Large-Scale Biosphere-Atmosphere Experiment in Amazonia. We found a range in the extent to which streamwater samples fell within the

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mixing space determined by potential flowpath end-members, suggesting that some water sources to streams were not sampled. The contribution of overland flow as a source of stream flow was greater in pasture watersheds than in forest watersheds of comparable size. Increases in overland flow contribution to pasture streams ranged in some cases from 0% in forest to 27–28% in pasture and were broadly consistent with results from hydrometric sampling of Amazon forest and pasture watersheds that indicate 17- to 18-fold increase in the overland flow contribution to stream flow in pastures. In forest, overland flow was an important contribution to stream flow (45–57%) in ephemeral streams where flows were dominated by stormflow. Overland flow contribution to stream flow decreased in importance with increasing watershed area, from 21 to 57% in forest and 60–89% in pasture watersheds of less than 10 ha to 0% in forest and 27–28% in pastures in watersheds greater than 100 ha. Soil solution contributions to stream flow were similar across watershed area and groundwater inputs generally increased in proportion to decreases in overland flow. Application of EMMA across multiple watersheds indicated patterns across gradients of stream size and land cover that were consistent with patterns determined by detailed hydrometric sampling.

Keywords Cattle pasture · Deforestation · Flowpaths · Principal components analysis · Overland flow · Soil solution

Introduction

The Amazon region encompasses the world's largest river basin and the largest area of extant tropical forest. Since the 1970s, more tropical forest has been cleared in the Amazon Basin than in any other tropical forest region and non-forest land now comprises nearly 20% of the Brazilian Amazon (Fearnside 2005; Simon and Garagorry 2005; INPE 2010). Cattle pasture, which historically has been the main driver for Amazon forest clearing, continues to be the most extensive use of cleared land in the Amazon (Buschbacher 1986; INPE 2010).

Conversion of Amazon forest to pasture has altered watershed hydrological processes by shifting the sources of water to stream flow to more rapid surface-dominated flowpaths because of soil compaction and decreased soil hydraulic conductivity associated with cattle grazing (Biggs et al. 2006; Moraes et al. 2006; Zimmermann et al. 2006; Germer et al. 2009, 2010). This alteration not only affects the transport of water to streams but has broader implications for watershed biogeochemistry because it alters the potential for transport of sediments and dissolved materials (Williams and Melack 1997; Neill et al. 2001; Davidson et al. 2004; Biggs et al. 2006; Germer et al. 2009). It also influences biogeochemical transformations as shifts in flowpaths modify water contact with reactive surfaces, redox conditions and chemical environments (Hill 1990; Creed et al. 1996; Boyer et al. 1997; Hill et al. 2000, McClain et al. 2003; Chaves et al. 2009). To date, the effects of land use on the distribution of water sources to streams have been quantified in several small catchments, but these have not been examined in multiple basins across different watershed sizes or across the diversity of topographic settings and soils that make up the Amazon basin as a whole.

End-member mixing analysis (EMMA) can identify the water sources within catchments that contribute to stream flow (Christophersen et al. 1990; Christophersen and Hooper 1992). This approach assumes that the chemistry of streamwater is the product of a mixture of discrete "sources" within catchments, in which solutes behave conservatively as they travel to streams. EMMA has been used to quantify groundwater, soil solution and overland flow sources to small streams in both temperate (Genereux et al. 1993; Mulholland 1993; Burns et al. 2001; Hooper 2001) and tropical (Elsenbeer et al. 1995; Chaves et al. 2008) settings. EMMA offers a way of using comparable datasets on the chemistry of water sources and streamwater to compare water sources to streams across multiple catchments. We compiled data on the chemistry of streamwater and the chemistry of specific hydrologic flowpaths from studies of 10 small Amazon catchments. These catchments represented a range of forest, pasture and mixed forest and pasture land use. We used EMMA to quantify the contribution of different hydrologic flowpaths to stream flows. Our objectives were to: (1) identify trends in water sources to stream flow across forest watersheds that could be determined from solute concentrations in streamwater and potential flowpath sources and compared with direct hydrometric measurements, (2) compare water sources in forest and pasture watersheds to identify the effects of land conversion on flowpath structure, and (3) examine how sources changed across a range of watershed scales.

Methods

Study sites

We derived data from published studies and unpublished results from sites examined under LBA that ranged from zero-order intermittent streams to third-order perennial streams (Fig. 1). Catchments ranged from 0.7 to 13,698 ha and included six forest watersheds, three pasture watersheds and one watershed that contained mixed forest and pasture. Soil types across sites were predominantly Ultisols with only one site (Vitória) on Oxisols (Table 1).

Nova Vida contained two pairs of second-order perennial forest and pasture streams (Neill et al. 2006). The catchments consisted of broad areas of rolling hills bisected by distinct floodplains 20–50 m wide. The pastures in both catchments were created directly from forest cleared in 1989. Bedrock was predominantly Pre-Cambrian granite and soils were predominantly Kandiudults and Paleudults.

Rancho Grande contained adjacent forest and pasture catchments that drained to 0-order streams (Chaves et al. 2008; Germer et al. 2009). The forest stream was ephemeral and flowed mostly during storms. The pasture stream was intermittent and flowed nearly continuously during the wet season. The pasture was cleared in 1985 and planted to pasture in 1986. The bedrock was predominantly granite and gneiss, which has eroded into a low relief landscape of flat valley floors with gently rolling slopes bound by steep ridges as high as 15.0 m. Streams originated in areas of low relief on the plateaus approximately 50–100 m upstream of larger perennial streams. Soils were Kandiudults.

Fazenda Vitória in Paragominas contained a large perennial first-order stream that drained a mixture of forest and pasture (Markewitz et al. 2001, 2004; Figueiredo et al. 2010). Forest was originally cleared for pasture in 1969. The catchment topography consisted of broad plateaus bisected by the 0-order stream channels and the first-order stream. The bedrock was predominantly granitic and soils were primarily Haplustoxes on plateaus and Plinthulstults on side slopes.

Juruena was an undisturbed forest catchment on Ultisols drained by a small, perennial first-order stream (Johnson et al. 2006). Topography was gently

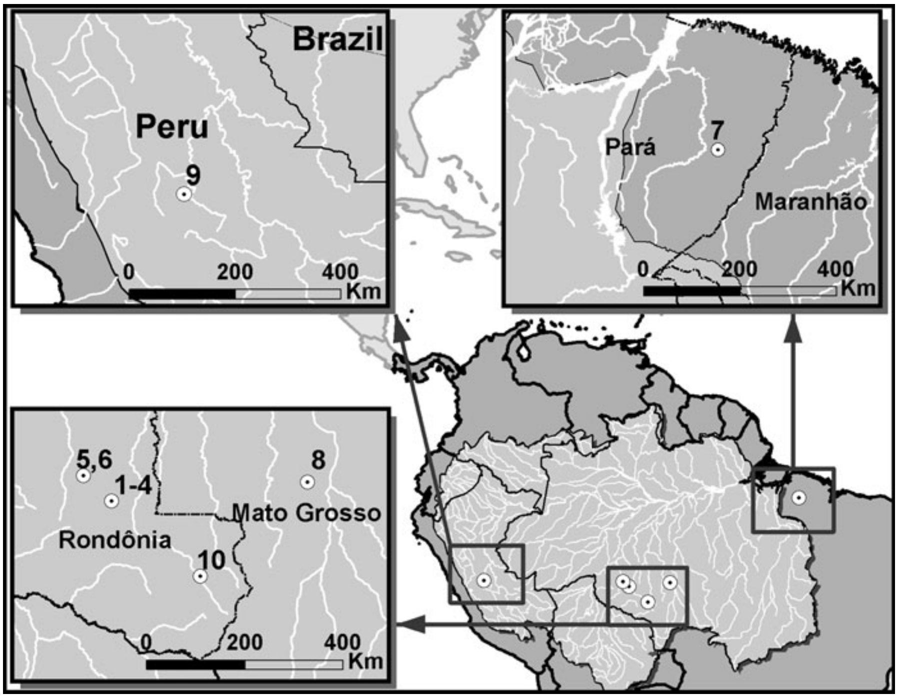

Fig. 1 Location of small watershed studies in the Brazilian Amazon Basin used in this study. The extent of the Amazon River drainage basin is highlighted. Numbers correspond to sites in Table 1

Table 1 Location and characteristics of catchments used in this study

No.	Location	Land cover	Area ha	Rainfall mm	Baseflow (l s^{-1})	Flow type, soil	Source
1	Nova Vida 1, Rondônia	Forest	1,740	1,939	15	Perennial, Ultisol	Neill et al. (2001)
2	Nova Vida 2, Rondônia	Forest	250	1,939	10	Perennial, Ultisol	Neill et al. (2001)
3	Nova Vida 1, Rondônia	Pasture	130	1,939	15	Perennial, Ultisol	Neill et al. (2001)
4	Nova Vida 2, Rondônia	Pasture	720	1,939	18	Perennial, Ultisol	Neill et al. (2001)
5	Rancho Grande, Rondônia	Forest	1.4	2,300	0	Ephemeral, Ultisol	Germer et al. (2009)
6	Rancho Grande, Rondônia	Pasture	0.7	2,300	<1	Intermittent, Ultisol	Germer et al. (2009)
7	Vitória, Pará	Mixed	13,698	1,803	800	Perennial, Oxisol	Markewitz et al. (2001)
8	Juruena, Mato Grosso	Forest	1.9	2,379	0.7	Perennial, Ultisol	Johnson et al. (2006)
9	La Cuenca, Perú	Forest	0.7	3,300	0	Ephemeral, Ultisol	Elsenbeer et al. (1996)
10	Nossa Senhora, Rondônia	Pasture	3.9	1,918	0	Ephemeral, Ultisol	Biggs et al. (2006)

Rainfall and baseflow were in the year that stream flow samples were collected. Ephemeral streams had flow during rain events. The intermittent stream had flow during the rainy season but not most of the dry season

undulating typical of the Brazilian shield on granitic bedrock and the stream was located in a narrow (0.5 m) riparian zone that originated at the base of the hillslope. Soils were Ultisols.

La Cuenca was an undisturbed forest catchment drained by a 1st-order stream, with a narrow valley floor, pronounced headwater gullies, and steep side slopes (Elsenbeer et al. 1992). Soils were Ultisols.

Nossa Senhora was a pasture catchment draining a hillslope that was deforested in the late 1970s and early 1980s (Biggs et al. 2006). There was no natural channel and compacted cattle paths routed overland flow to the base of the hillslope. The catchment contained gentle slopes of 1–3% with a steeper slope to a 25-m wide near-stream zone. The catchment was on gneissic bedrock and Paleudults.

Data sources

We assembled cation and anion concentration data from streamwater and from catchment sources of water that were potential sources of stream flow at each site. These included rain, groundwater, soil solution, throughfall and overland flow (Figs. S1–S7 in Supplementary material). The location of groundwater sampling varied among plateau, the riparian zone and springs. All potential sources were sampled during the same time period at each site except for the two exceptions noted below. Streamwater samples reflected the representative flows at each site and were predominantly baseflow in perennial streams (Nova Vida, Vitória, Juruena, La Cuenca) and stormflow in ephemeral streams (Rancho Grande, Nossa Senhora).

At Nova Vida, potential forest and pasture sources sampled were rain, groundwater and soil solution at 30 and 100 cm collected with tension lysimeters. Throughfall was sampled in forest and overland flow was sampled in pasture. No overland flow was captured by collectors in the forest. All Nova Vida water chemistry data spanned seven water years (1994–2001) during which periodic samplings were conducted both during the rainy and dry seasons (Neill et al. 2001). Streamwater samples were collected by grab sampling predominantly during baseflows across rainy and dry seasons.

At Rancho Grande, sources of stream flow sampled in both forest and pasture were rain, groundwater, soil solution from tension lysimeters at depths of 20 and 100 cm and overland flow. Throughfall was also sampled in the forest. All Rancho Grande water chemistry data spanned one rainy season from August 2004 to April 2005 (Chaves et al. 2008; Germer et al. 2009). Streamwater samples were collected during events by Isco® automatic water samplers over periods of three to about 24 h when water was flowing.

At Fazenda Vitória, we sampled rain, groundwater from upland, near-stream and hyporheic zones, soil solution collected with tension lysimeters at a depth of 20 cm and overland flow (Markewitz et al. 2004; Moraes et al. 2006). Groundwater, soil solution and overland flow were collected in both forest and pasture portions of the watershed. All Vitória water chemistry data spanned seven water years (1994–2001). Streamwater samples were collected by grab sampling across streamwater levels during the rainy season (Markewitz et al. 2001). These samples represented predominantly rainy season baseflow but included some samples at moderate stormflows.

At Juruena, sources sampled were rain, groundwater (including spring water), throughfall and overland flow. Because no soil solution data were available, soil solution collected in a forested watershed on similar soils at Fazenda Nova Vida was tested as potential end-member. All water chemistry data for Juruena were collected during two years (Nov. 2003 to Nov. 2005). Streamwater sampling was by grab sampling of baseflow at an average interval of 10 days, and of stormflow for three rain events during that period (Johnson et al. 2006).

At La Cuenca, we sampled rain, groundwater, soil solution at a depth of 30 cm with tension lysimeters, throughfall and overland flow. Stream water chemistry was based on sampling stormflow during five rain events between March and September 1988 (Elsenbeer et al. 1996).

At Nossa Senhora, catchment sources were groundwater and overland flow. Nossa Senhora water chemistry was from stormflow during six rain events between September and November 2002 (Biggs et al. 2006). Stormflow was collected from water draining to the base of the hillslope. Because our initial EMMA results suggested an unsampled end-member and because no in situ soil solution chemistry data were available for Nossa Senhora, we added data on soil solution from the Rancho Grande pasture watershed on a similar Ultisol as a potential end-member (Biggs et al. 2006).

Data analysis

We used a multivariate end-member mixing analysis technique based on principal component analysis (PCA) (Christophersen and Hooper 1992; Hooper 2003) to identify potential sources of stream flow (i.e., the end-members), and to calculate their relative contribution. The purpose of the PCA is to find a "lower-dimensional" space, U, which allows for the use of an over-determined set of equations in which more solute tracers than necessary are used to solve for the end-members proportions, while incorporating most of the variance associated with the tracers. The dimensionality of U space, and hence the maximum number of end-members that can be resolved, is determined by the number of vectors (m) retained from the PCA. In this study, we retained two vectors from the PCAs for each site, which allowed solving for a maximum of three end-members, and to conveniently display and analyze the mixing space as a two-dimensional "mixing diagram." The decision to solve for either two or three end-members for a particular set of observations was based on the spread of the data between potential end-members on the mixing diagrams and information about the nature of the flow data (i.e., base versus stormflow).

For each site, the stream concentration data (n) for the solutes (p) were standardized by centering them about their means and dividing by their respective standard deviations. The median concentrations of each of the measured potential end-members were also standardized by subtracting the means and dividing by the standard deviations of the stream observations. The standardized stream data and potential end-member medians were projected onto the m-dimensional U space by the orthogonal projection given by

$$\mathbf{U} = \mathbf{X}\mathbf{V}^{\mathbf{T}} \quad (1)$$

where $\mathbf{U}$ is the $n \times m$ projected data matrix, $\mathbf{X}$ is the $n \times p$ standardized data matrix, and $\mathbf{V}$ is the is the $m \times p$ matrix of the retained eigenvectors. The projected end-members that best bounded the stream data in U space were chosen as end-members for the mixing models in each watershed.

The proportion of the chosen end-member in each streamwater observation was obtained by solving the following system of linear equations:

$$1 = x + y + z \quad (2)$$

$$\mathrm{SW}_{\mathrm{U1}} = x\mathrm{EM}_{1\mathrm{U1}} + y\mathrm{EM}_{2\mathrm{U1}} + z\mathrm{EM}_{3\mathrm{U1}} \quad (3)$$

$$\mathrm{SW}_{\mathrm{U2}} = x\mathrm{EM}_{1\mathrm{U2}} + y\mathrm{EM}_{2\mathrm{U2}} + z\mathrm{EM}_{3\mathrm{U2}} \quad (4)$$

where x, y, and z are the unknown proportions of each end-member; $\mathrm{SW}_{\mathrm{U1}}$ and $\mathrm{SW}_{\mathrm{U2}}$ are the coordinates in U space, $U1$ and $U2$, for a streamwater observation. Likewise, $\mathrm{EM}_{n\mathrm{U1}}$ and $\mathrm{EM}_{n\mathrm{U2}}$ are the coefficients in U space for the nth end-member. Equations 2–4 depict the case for a three end-member mixing scenario. Because of various sources of error, such as non-conservative solute behavior, time-dependent end-member variability, the existence of unsampled end-members, and/or analytical uncertainty, some stream observations lie outside the mixing domain defined by the end-members chosen as sources of stream flow. The solutions to the above equations in those cases result in end-member fractions for which negative values are found. To circumvent that problem, the outlier observations were perpendicularly projected to the line joining the two non-zero end-members and solved geometrically in *U* space as binary mixtures of these two end-members (Liu et al. 2004).

To examine pattern of sources across watersheds of different sizes, we plotted the EMMA-derived flowpath contributions against watershed area. Flowpath contributions were determined two ways: (1) as percent of total water yield from the watershed, and (2) as total water yield. Comparisons of total yield allowed us to compare contributions in pastures where the total water moving in different flowpaths (e.g., overland flow) was much greater than from forest. The contributions were determined only during the period of streamwater sampling. For the smallest watersheds with ephemeral streams, this amounted to the time surface flow was present.

All data analyses were carried out in R version 2.7.0 (R Development Core Team 2008).

Results

Solute and end-member selection

In most cases the solutes Na^+, K^+, Mg^{2+} and Ca^{2+} provided the clearest two dimensional projections of the mixing space (Table 2). In two cases (Nova Vida and Rancho Grande pastures) addition of a fourth solute did not explain additional variation. In several other cases, inclusion of SO_4^{2-} (Vitória), Si (La Cuenca) or Cl^- (Nossa Senhora) improved mixing space projections (Table 2). Groundwater was an end-member in every catchment and soil solution was an end-member in 9 of 10 catchments (Table 2). Overland flow was a third end-member in the four Rondônia pasture catchments and either overland flow or throughfall were end-members in the smallest forest catchments (Table 2).

Individual watershed end-member mixing

For the larger of the two forest watersheds at Nova Vida, most of the stream observations were distributed between soil solution and groundwater end-members (Fig. 2). EMMA identified groundwater as the major contributor to stream flow (94%), with the rest attributed to soil solution (Table 3). For the smaller forest watershed at Nova Vida, stream observations also fell between the soil solution and groundwater end-members, although with considerably more scatter. Groundwater was the largest contributor to stream flow (62%), while soil solution provided the remaining flow (38%) (Table 3).

At both pasture watersheds at Nova Vida, the majority of stream observations were bounded by overland flow, shallow soil solution and riparian groundwater (Fig. 2). The EMMA solutions for these two pasture catchments were nearly identical. Estimated contributions to flow from overland flow were 27–28%, from groundwater 26–30%, and from soil solution 43–46% (Table 3).

In the forest watershed at Rancho Grande, stream observations for the first (“early”) and second (“late”) half of the rainy seasons were best bound by throughfall, groundwater, and shallow soil solution (Fig. 2). In the pasture, observations were distributed mostly between overland flow and groundwater, with less variability in streamwater tending towards soil solution (Fig. 2). Estimated contributions to flow for the entire rainy season in the Rancho Grande forest were 57% from throughfall, 24% from groundwater and 19% from shallow soil solution (Table 3). In the pasture watershed at Rancho Grande, overland flow dominated stream flow at 60%, groundwater contribution was 35%, and soil solution was 5% (Table 3).

In the mixed land use watershed at Vitória, the set of end-members that bounded the largest number of stream observations in the mixing diagram were upland groundwater, near stream groundwater and pasture overland flow (Fig. 2). The EMMA solution found flow contributions at 40% from upland groundwater, 23% from near stream groundwater, and 37% from pasture overland flow (Table 3).

Table 2 Chemical tracers and end-members selected for EMMA analysis at each site

No.	Location	Land cover	Tracers used in EMMA	End-members selected
1	Nova Vida Site 1, RO	Forest	Na^+, K^+, Mg^{2+}, Ca^+	Riparian groundwater, soil solution
2	Nova Vida Site 2, RO	Forest	Na^+, K^+, Mg^{2+}, Ca^+	Riparian groundwater, soil solution
3	Nova Vida Site 1, RO	Pasture	K^+, Mg^{2+}, Ca^+	Overland flow, riparian groundwater, soil solution
4	Nova Vida Site 2, RO	Pasture	K^+, Mg^{2+}, Ca^+	Overland flow, riparian groundwater, soil solution
5	Rancho Grande, RO	Forest	Na^+, K^+, Mg^{2+}, Ca^+	Throughfall, groundwater, soil solution
6	Rancho Grande, RO	Pasture	K^+, Mg^{2+}, Ca^+	Overland flow, groundwater, soil solution
7	Vitória, PA	Mixed	SO_4^{2-}, K^+, Mg^{2+}, Ca^+	Upland groundwater, near-stream groundwater, pasture overland flow
8	Juruena, MT	Forest	Na^+, K^+, Mg^{2+}, Ca^+	Spring groundwater, overland flow, soil solution
9	La Cuenca, Peru	Forest	K^+, Si, Ca^+	Overland flow, groundwater, soil solution
10	Nossa Senhora, RO	Pasture	Cl^-, Na^+, K^+	Overland flow, groundwater, soil solution

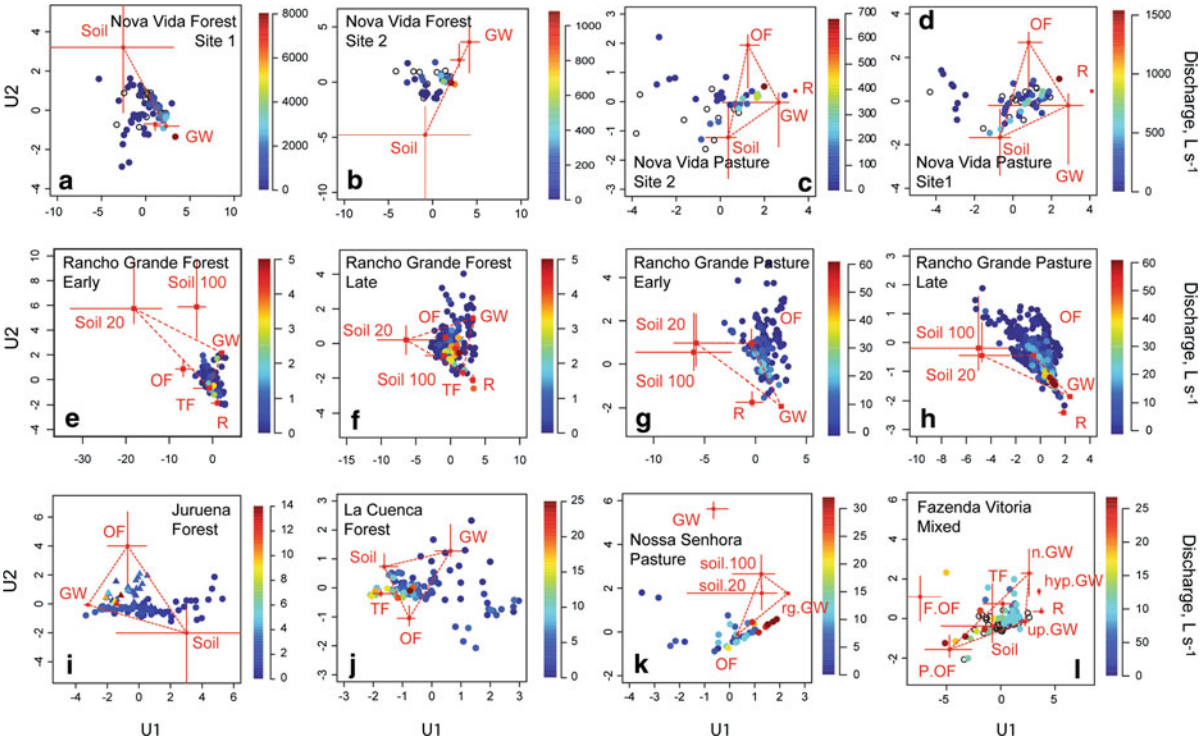

Fig. 2 Two-dimensional mixing diagrams created by EMMA for each watershed. Points represent streamwater concentrations and are color coded by discharge (scale bar units are l s^{-1}) Abbreviations are GW (groundwater), OF (overland flow), R (rain), TF (throughfall). Soil 20 and Soil 100 indicate soil solution collected in lysimeters at 20 and 100 cm depth. For Juruena, stream samples during stormflow are designated with triangles. For Nossa Senhora, rgGW indicates groundwater collected at Rancho Grande. For Fazenda Vitória, overland flow was from forest (F) and pasture (P), and groundwater was from upland (up), a near-stream zone (ns) and the stream hyporheic zone (hyp)

Table 3 Proportions of end-members derived from the EMMA solution at each site

No.	Location	Land cover	Overland flow/Troughfall (%)	Groundwater (%)	Soil solution (%)
1	Nova Vida, RO	Forest	0	94	6
2	Nova Vida, RO	Forest	0	62	38
3	Nova Vida, RO	Pasture	28	26	46
4	Nova Vida, RO	Pasture	27	30	43
5	Rancho Grande, RO	Forest	57	24	19
6	Rancho Grande, RO	Pasture	60	35	5
7	Vitória, PA	Mixed	37	63	0
8	Juruena, MT	Forest	21[a] (0)[b]	57[a] (60)[b]	22[a] (40)[b]
9	La Cuenca, Peru	Forest	45	28	27
10	Nossa Senhora, RO	Pasture	89	11	<1

For Juruena, separate analyses were performed for [a] stormflow and [b] baseflow

The mixing diagram for the forest watershed at Juruena showed most of the baseflow stream observations distributed between the groundwater and the soil solution end-members (Fig. 2). Stormflow observations appeared chemically distinct and plotted closer to the groundwater end-member on the mixing diagram but with a small contribution from overland flow (Fig. 2). To solve the EMMA we used groundwater, soil solution, and overland flow end-members. Baseflow observations were solved as binary mixtures of the soil and groundwater end-members given the distribution of the observation between these two components and the physical impossibility of overland flow to act as a source outside of precipitation events in this small (1.9 ha) watershed. Stormflow was solved as mixture of all three end-members. Groundwater was as the main contributor to flow at approximately 60% during baseflow and stormflow, while soil solution provided the remaining 40% of baseflow (Table 3). The estimated contribution of overland flow to total stormflow was 21%.

In the forest watershed at La Cuenca, overland flow, soil solution, and groundwater were the end-members that bounded the greatest number of stream observations in the mixing diagram (Fig. 2). The calculated contributions to flow were 45%, 27%, and 28% respectively (Table 3).

In the pasture watershed at Nossa Senhora, most streamwater observations fell outside any potential mixing domain that could be created with any of the end-members incorporated in the analysis, including those from the very similar pasture watershed at Rancho Grande (Fig. 2). Although, most stream observations plotted close to the overland flow end-member, the observations tended towards the chemical signature of the Rancho Grande groundwater rather than that of groundwater. We solved the EMMA using Nossa Senhora overland flow, the Rancho Grande groundwater and soil solution end-members. The contributions to flow calculated in this manner were 89% from overland flow, 11% from groundwater, and was less than 1% from soil solution.

Patterns as a function of watershed size

The contribution of overland flow as a source of stream flow was greater in pasture watersheds than in forest watersheds of comparable size. This was true when contributions were considered as: (1) a fraction of total flow (Fig. 3) and (2) as the instantaneous water yield over the time that flow was logged at each site (Fig. 4). There was a general trend toward lower contribution from overland flow in larger watersheds in both forest and pasture but these were not statistically significant. The contribution from soil solution remained relatively constant across watershed size. For groundwater, there was no consistent pattern with land use. Groundwater as a proportion of total flow increased significantly with watershed size only in forest (Fig. 3).

Discussion

Application of EMMA to watershed studies is most commonly performed in small well-instrumented and

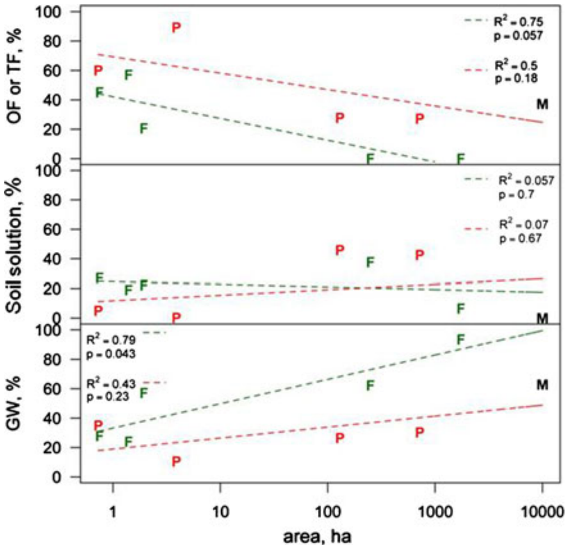

Fig. 3 Proportions of throughfall or overland flow, soil solution and groundwater end-members as a percentage of total stream flow plotted against watershed area for all sites. Land cover is forest (F), pasture (P) or mixed (M)

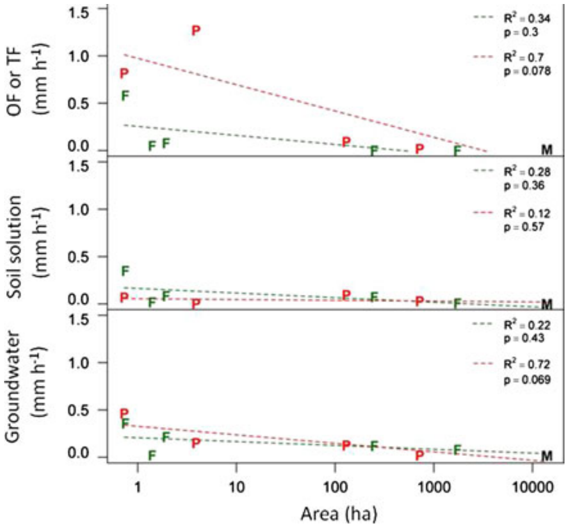

Fig. 4 Instantaneous water yield (mm h^{-1}) of throughfall or overland flow, soil solution and groundwater end-members plotted against watershed area for all sites. Land cover is forest (F), pasture (P) or mixed (M)

well-sampled watersheds where a qualitative understanding of source contributions to stream flow is developed from a detailed understanding of basin characteristics and hydrometric sampling (Elsenbeer and Lack 1996; Hooper 2001; Chaves et al. 2008). In these cases, EMMA can be used to test specific hypotheses about sources which may include flowpaths of stream flow and to determine if all potential sources have been identified in the case that stream flow samples fall outside the mixing space (Hooper 2001).

We found a wide range in the extent to which streamwater samples fell within the mixing space determined by the sources for which solute concentrations were available. For example, streamwater samples in forests at Nova Vida, Rancho Grande and Juruena and the mixed watershed at Vitória were well constrained by the sources sampled, but the forest at La Cuenca and the pastures at Nova Vida, Rancho Grande and Nossa Senhora were not. This suggests potentially (1) the existence of sources of stream flow in these watersheds that were not sampled, or (2) sampling of sources that was insufficient to capture the true range of variability in space and time. In the case of the Nova Vida pastures, for example, greater variation in the chemistry of overland flow or soil solution might capture some of the points outside the mixing space. While sampling of end members occurred concurrently with sampling of stream flow, few flowpaths were sampled year-round at a frequency sufficient to capture the annual range of solute concentrations. In these cases where the mixing diagrams did not capture the full range of streamwater solute concentrations, EMMA indicates which additional sources might contribute and which sources may not have been adequately sampled. We did not weigh our streamwater samples by flow. This analysis, therefore, reflects the stream chemistry under the hydrologic conditions in which streams were sampled (predominantly baseflow in permanent streams, storm flows in ephemeral streams) and does not adequately indicate streamwater sources under storm flows in the larger streams because these conditions were inadequately sampled.

We found that the proportional contribution to stream flow of water with chemical characteristics of overland flow was higher in pasture than in forest and that water yields (mm $year^{-1}$) from pasture were also higher. This was consistent 1) with measurements of soil hydraulic properties from Amazon forest and pasture that indicate that conversion to cattle pasture leads to reduction of surface soil infiltrability and hydraulic conductivity to the extent necessary to generate overland or near-surface horizontal flows

(Zimmermann et al. 2006) and 2) with direct hydrometric measurements of greatly enhanced stormflow from Amazon pasture watersheds (Biggs et al. 2006; Moraes et al. 2006; Germer et al. 2009, 2010). Moraes et al. (2006) and Germer et al. (2009) found 17- to 18-fold increases in overland flow in small (∼1 ha) pasture compared with forest watersheds in Vitória and Rancho Grande.

The wide range of EMMA-derived overland flow contributions to stream flow (0–45%) in the forested watersheds was unexpected. We attributed this in part to the range in catchment size of our sites, and in part to the wide range in permeability changes with depth. The highest contributions of overland flow occurred at Nossa Senhora, Rancho Grande and La Cuenca. At La Cucena the decrease of permeability with depth is among the most pronounced on record (Elsenbeer 2001). Given high rainfall totals and intensities, these streams captured a small overall percentage of the watershed runoff. For example, overland flow in the forest stream at Rancho Grande made up only 3–4% of combined streamflow and groundwater recharge (Chaves et al. 2009). So while the contribution of overland flow to stream flow in these streams was high and dominated by surficial flows, the total flow in these streams was small. The perennial streams in the larger watersheds at Nova Vida (watershed areas of 250–1,740 ha) captured larger flows from groundwater and any storm-derived flow from surficial flowpaths were small in comparison to flows derived from groundwater and soil solution.

At Nossa Senhora, the groundwater table was several meters below the ground surface at the sampling point and direct observations of runoff processes during the storms suggested that all of the water sampled in the pasture watershed was generated by overland flow. Any contribution of groundwater determined from EMMA likely reflects the temporal variations in the chemical composition of overland flow, rather than actual contribution of groundwater to stream flow. The EMMA suggested that the contribution of soil water to stormflow from the hillslope was minimal and dominated by overland flow. Given these observations, appropriate endmembers for the Nossa Senhora site might include different types of overland flow that interacted with chemically distinct surface materials, such as cattle feces, vegetation, and surface litter.

The small spring-fed stream at Juruena was somewhat different in that <5% of annual stream flow was stormflow (Johnson et al. 2006). Using a purely hydrometrics approach resulted in an estimated runoff coefficient of 3% for 27 storms (Johnson et al. 2007). Using electrical conductivity as a tracer for hydrograph separation and the TRANSEP model (Johnson et al. 2007) found that stormflow averaged 4% across 14 rain events. The hydrochemical data required for the application of EMMA was only available for three storms for the Juruena catchment. While stormflow comprised <5% of total annual stream flow at Juruena, Johnson et al. (2007) found stormflow consisted of 79% pre-event water and 21% event water. This TRANSEP-based estimate was consistent with the EMMA results for Juruena, which estimated the contribution of overland flow to total stormflow also at 21%. The Juruena stream was the exception to the finding that the groundwater contribution to stream flow increased with watershed size.

Several constraints limit the utility of EMMA for multiple watershed comparisons. First, the use of EMMA requires relatively intensive sampling of multiple flowpaths and sampling both flowpaths and streamwater at a frequency sufficient to capture the majority of seasonal variation in solute chemistry. Second, EMMA requires analysis of multiple solutes, so it is not possible to apply EMMA to studies generally conducted with other objectives that report results for only a single element or a limited set of elements. Third, EMMA assumes that solutes are conservative as they travel both from watersheds to streams and downstream in stream channels (Christophersen and Hooper 1992). While it is widely known that soils and stream channels play major roles in transforming concentrations of biologically active solutes (Qualls 2000; Peterson et al. 2001), fewer experiments have been conducted on elements such as calcium and potassium that along with chloride are typically components of EMMA. Despite these limitations, our application of EMMA across multiple watersheds indicated that EMMA revealed patterns across gradients of stream size and land cover that were consistent with patterns determined by detailed hydrometric sampling.

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